

DESCRIPTION

CHLORINATED POLYOLEFINS AND PROCESS FOR THEIR PRODUCTION

5 Cross-Reference to Related Application

This application is an application filed under 35 U.S.C. § 111(a) claiming benefit pursuant to 35 U.S.C. § 119(e)(1) of the filing date of the Provisional Application 60/412,793 filed September 24, 2002, pursuant to 35 U.S.C. § 111(b).

10 Technical Field

) The present invention relates to chlorinated polyolefins and to a process for their production. In particular, the invention relates to chlorinated 15 polyolefins which are suitable as starting materials for crosslinked rubber and thermoplastic elastomer having not only excellent oil resistance, heat resistance and the like, but also excellent low-temperature rubber elasticity and compression set, and to a process for 20 their production.

Background Art

) Chlorinated polyolefins are chlorinated compounds obtained by chlorination of polyolefins such as 25 polyethylene. Chlorinated polyolefins are commonly used as modifiers for ABS resins or polyvinyl chloride resins or as wire sheaths, but in recent years they are also coming into wider use as crosslinked rubbers or thermoplastic elastomers for automobile parts and industrial parts.

30 Because of the oil resistance, solvent resistance, weather resistance and flexibility characteristic of chlorinated polyolefins, they are also used as hoses or sheets, packings, automobile constant velocity universal joint boots and the like. Such uses also require 35 additional properties such as satisfactory heat resistance, ozone resistance, low-temperature rubber elasticity, compression set and fatigue strength.

Chlorinated polyolefins have conventionally been produced by chlorinating polyolefin powder in aqueous suspension while controlling the reaction temperature, chlorine content, etc. Various proposals have been set forth for such aqueous suspension methods, in order to obtain a uniform chlorinated polyolefin powder and in order to prevent agglomerating during the chlorinated reaction and maintain the powder particle size.

Surfactants or inorganic substances are commonly added as anti-aggregation agents in order to prevent agglomerating of particles during the reaction. On the other hand, when a copolymer of ethylene and an α -olefin is used as the starting material, a higher proportion of the α -olefin tends to result in lower crystallinity, and the increased number of free chains promotes agglomerating during the chlorination reaction. A production method known as a solution to this problem comprises a first step of chlorination at a temperature lower than the crystal melting point of the polyolefin starting material, a second step of heat treatment in the absence of chlorine at a temperature higher than the crystal melting point, and a third step of chlorination up to the final chlorine content at a temperature below the temperature of the second step and below the crystal melting point (see, for example, Japanese Unexamined Patent Publication No. 3-66325).

However, the effect of satisfactorily preventing agglomerating and maintaining the powder particle size depends on preventing unwanted crystal residue or a relatively poor level of non-uniformity, and it has been difficult to achieve uniform chlorinated polyolefins with excellent properties by the method described above.

It is also well known that polymerized polyolefin powder has a given range of particle size distribution and that differences in molecular weight and density are found between the particle sizes. The uniformity of a

chlorinated polyolefin depends primarily on the uniformity of the polyolefin starting material, and methods are known for obtaining uniform chlorinated polyethylene by adjusting the particle size of the 5 polyolefin starting material (see, for example, Japanese Unexamined Patent Publication No. 8-59737).

However, while improvement toward a more uniform product is achieved by narrowing the particle size distribution of the polyolefin powder, the more serious 10 problem of variation within each particle is not affected, and these obtained chlorinated polyolefins therefore remain unsatisfactory in several of their properties.

Disclosure of Invention

It is therefore an object of the present invention 15 to provide uniform chlorinated polyolefins which can give crosslinked rubbers and thermoplastic elastomers with excellent low-temperature rubber elasticity, compression set and fatigue strength, and a process for their 20 production.

As a result of much diligent research directed 25 toward solving the aforementioned problems, the present inventors have completed the present invention based on the discovery that these problems can be overcome by employing a production process wherein polyolefin powder having a mean particle size of no greater than 500 µm, obtained by pulverizing a melted and kneaded solid, is used as the starting material for chlorination.

Thus, the invention relates to the following (1) to 30 (17).

(1) A process for production of a chlorinated polyolefin comprising a step of melting and kneading a polyolefin and then molding it to obtain a solid, a step of pulverizing the solid into powder having a mean 35 particle size of no greater than 500 µm, and a step of chlorinating the powder.

(2) A process for production of a chlorinated polyolefin according to (1) above, wherein the chlorinating step further comprises a first step of chlorination at above the crystal melting start 5 temperature and more than 10°C below the crystal melting peak temperature of the polyolefin starting material as determined by DSC, a second step of interrupting the chlorine supply and performing heat treatment by heating to a temperature which is higher than 5°C below the 10 crystal melting peak temperature, and a third step of rechlorination at a temperature above the crystal melting start temperature of the chlorinated polyolefin after the heat treatment step.

(3) A process for production of a chlorinated 15 polyolefin according to (1) or (2) above, wherein the polyolefin is polyethylene.

(4) A process for production of a chlorinated polyolefin according to (3) above, wherein the polyethylene is linear low-density polyethylene.

(5) A process for production of a chlorinated polyolefin according to (3) or (4) above, wherein the 20 density of the polyethylene is 0.90-0.93.

(6) A process for production of a chlorinated polyolefin according to any one of (3) to (5) above, 25 wherein the polyethylene is polyethylene with a weight-average molecular weight (M_w) and number-average molecular weight (M_n) ratio (M_w/M_n) of no greater than 3.0 as measured by gel permeation chromatography.

(7) A chlorinated polyolefin produced by a process 30 according to any one of (1) to (6) above, wherein the chlorinated polyolefin has a crystal heat of fusion of no greater than 30 J/g according to DSC.

(8) A chlorinated polyolefin according to (7) above, wherein the chlorine content is 15-45 wt%.

(9) A chlorinated polyolefin according to (7) or (8) above, wherein the elongation based on a tensile test is 35 1500% or greater, and the glass transition temperature is

no higher than -25°C.

(10) A chlorinated polyolefin according to any one of (7) to (9) above, wherein the chlorinated polyolefin is chlorinated polyethylene.

5 (11) A chlorinated polyolefin crosslinkable composition comprising 100 parts by weight of a chlorinated polyolefin according to any one of (7) to (10) above, 0.5-20 parts by weight of an acid acceptor, 10-80 parts by weight of a reinforcer, 0.5-10 parts by 10 weight of a crosslinking agent and 5-70 parts by weight of a plasticizer.

(12) A crosslinked chlorinated polyolefin obtained by crosslinking a chlorinated polyolefin crosslinkable composition according to (11) above.

15 (13) A crosslinked chlorinated polyolefin according to (12) above, wherein the temperature at which the relative modulus (RM) = 2 by a cold flex test is no higher than -25°C.

20 (14) A crosslinked chlorinated polyolefin according to (12) above, wherein the temperature at which the relative modulus (RM) = 5 by a cold flex test is no higher than -40°C.

) 25 (15) A crosslinked chlorinated polyolefin according to (12) above, wherein the temperature at which the relative modulus (RM) = 10 by a cold flex test is no higher than -45°C.

(16) An automobile boot or hose employing a crosslinkable composition or crosslinked polyolefin according to any one of (11) to (15) above.

30 (17) An industrial hose, sheet or packing employing a crosslinkable composition or crosslinked polyolefin according to any one of (11) to (15) above.

35 According to the present invention it is possible to provide chlorinated polyolefins which can be used as starting materials for crosslinked rubbers and thermoplastic elastomers exhibiting excellent low-temperature rubber elasticity, compression set and

fatigue strength, which are particularly useful in the fields of automobiles, household electrical appliances, building materials and the like.

5 Best Mode for Carrying Out the Invention

The chlorinated polyolefin production process of the invention is characterized by comprising a step of melting and kneading a polyolefin and then molding it to obtain a solid, a step of pulverizing the solid into powder having a mean particle size of no greater than 500
10 μm, and a step of chlorinating the powder.

Specifically, the production process is characterized by melting and kneading polyolefin powder or pellets, and then molding this into a solid which is then pulverized to a mean particle size of no greater
15 than 500 μm to prepare a powder to be used as a starting material.

Here, the "solid" referred to here may be pellets, beads or the like obtained by melting, kneading and molding, and although the size and shape or the like are not particularly restricted, a smaller size is preferred because of the pulverization in the subsequent step. If the mean particle size, represented as the 50% particle size based on weight, of the polyolefin powder used in the chlorination step of the process of the invention is greater than 500 μm, the low-temperature rubber elasticity will be impaired.
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25

The step of melting and kneading the polyolefin starting material and molding it into a solid is usually carried out using an extruder or the like, but there are no particular restrictions on the method so long as one or more starting materials selected from among powder obtained from a polyolefin production process and already melted, kneaded and molded solids, are first melted and subjected to a step of physical shearing followed by
30
35 cooling to hardness to achieve the desired homogeneity of the molding material.

The melting and kneading of the polyolefin may also be carried out by an ordinary method, and it will generally be conducted at or above the melting point of the polyolefin, but here as well, the process and conditions are not particularly restricted so long as the desired homogeneity of the molding material can be achieved.

The pulverization of the obtained solid is not particularly restricted, although a shearing-type pulverizer is more suitable for pulverization of polyolefins than an impact-type pulverizer, and there are no particular restrictions on the method or type of pulverizer used so long as the mean particle size of the powder after pulverization is no greater than 500 μm .

As examples of polyolefins to be used for the invention there may be mentioned α -olefin homopolymers of ethylene, propylene, butene-1, pentene-1, hexene-1, octene-1, 4-methylpentene-1 and the like, and copolymers of ethylene and α -olefin or copolymers of 2 or more different α -olefins which are crystalline polymers. Such copolymers include random and block copolymers. The polyolefins may be powders obtained from a production process or pellets obtained by prior melting and kneading, and two or more different polyolefins may be used in admixture for the melting and kneading.

The polyolefin is preferably polyethylene. Polyethylene for the purpose of the invention includes not only ethylene homopolymer but also ethylene copolymer copolymerized with an α -olefin, such as medium-density or linear low-density polyethylene. The polyethylene is preferably linear low-density polyethylene, and the density of the polyethylene is preferably 0.90-0.93. Also, the polyethylene preferably has a weight-average molecular weight (M_w) and number-average molecular weight (M_n) ratio (M_w/M_n) of no greater than 3.0 as measured by

5 gel permeation chromatography. The Mw/Mn ratio is more preferably between 1.0 and 2.9, and especially between 1.5 and 2.8. If the Mw/Mn ratio is less than 1.0 the workability may be reduced, and if it exceeds 3.0 the mechanical strength may be reduced.

10 As examples of polyolefins satisfying the conditions described above there may be mentioned those obtained by polymerization using a metallocene catalyst comprising a metallocene compound of a transition metal selected from Group IVB of the Periodic Table, and an organic aluminoxy compound. As examples of transition metals selected from Group IVB of the Periodic Table there may be mentioned zirconium, titanium, hafnium and the like. As examples of organic aluminoxy compounds there may be mentioned conventional known aluminoxanes obtained by reaction conducted by adding an organic aluminum compound such as trialkylaluminum to a compound containing water of adsorption or a salt containing water of crystallization, for example, aluminum sulfate hydrate or magnesium 15 chloride hydrate suspended in an aromatic hydrocarbon solvent, although there is no restriction to such compounds.

20 The step of chlorination of the powder preferably comprises a first step of chlorination at above the crystal melting start temperature and more than 10°C below the crystal melting peak temperature of the polyolefin starting material as determined by DSC, a second step of interrupting the chlorine supply and performing heat treatment by heating to a temperature which is higher than 5°C below the crystal melting peak 25 temperature, and a third step of rechlorination at a temperature above the crystal melting start temperature of the chlorinated polyolefin after the heat treatment step.

30 In the first step of chlorination, chlorination at a temperature below the crystal melting start temperature will tend to promote non-uniformity of chlorination and

the resulting chlorinated polyolefin will sometimes lack flexibility. On the other hand, chlorination at a temperature more than 10°C below the crystal melting peak temperature is preferred. Chlorination at a higher
5 temperature will tend to promote aggregation and agglomerating of the reacting particles, resulting in non-uniform chlorination and often yielding a product with unsatisfactory elongation or low-temperature properties. Likewise, the heating in the second step at
10 a temperature exceeding 5°C below the crystal melting peak temperature is preferred. If the heating is carried out at a lower temperature, the crystals will tend to remain, often not only making it difficult to obtain amorphous chlorinated polyethylene but also resulting in
15 non-uniformity even if crystalline chlorinated polyethylene is obtained. Similarly, chlorination in the third step at a temperature below the crystalline melting start temperature of the chlorinated polyolefin after the heat treatment step will also tend to result in residue
20 of the crystals, often not only making it difficult to obtain amorphous chlorinated polyethylene but also resulting in non-uniformity even if crystalline chlorinated polyethylene is obtained.

The chlorination step is preferably conducted so
25 that the final chlorine content in the first step is no greater than 90%.

For chlorination by an aqueous suspension method, there may be added conventional known agents, such as a dispersing agent to wet the polyolefin powder and
30 disperse it in water, or an anti-agglomerating agent added either before or during the reaction for the purpose of preventing aggregation of the reaction particles during the chlorination reaction.

As examples of dispersing agents there may be
35 mentioned anionic surfactants such as alkylbenzenesulfonates, alkynaphthalenesulfonates, alkyldiphenylether sulfonates, dialkylsulfosuccinates,

alkylphosphates, alkylsulfuric acid esters,
naphthalenesulfonate formalin condensates and
polyoxyethylenealkylsulfuric acid esters, nonionic
surfactants such as sorbitan fatty acid esters,
5 polyoxyethylene sorbitan fatty acid esters,
polyoxyethylene alkylallyl ethers, polyoxyethylenealkyl
ethers and oxyethylene-oxypropylene block polymers, or
polyvinyl alcohol, carboxymethylcellulose, starch,
gelatin or the like.

10 As examples of anti-agglomerating agents there may
be mentioned protective colloids such as polyacrylic
acid, copolymers of maleic anhydride and styrene or
methylvinyl ether, or polyacrylamide,
15 polyvinylpyrrolidone, or the like, surfactants such as
polystyrenesulfonate, sodium alkylallylsulfonate formalin
condensate, diphenylmethylenesulfonic acid formalin
condensate, isobutylene-styrene copolymer sulfonic acid
ester, β -naphthalenesulfonate formalin condensate and
polyacrylates, or inorganic powders such as talc or
20 silica.

The crystals of the chlorinated polyolefin obtained
by the production process of the invention preferably
have a crystal heat of fusion of no greater than 30 J/g
and more preferably no greater than 20 J/g according to
25 DSC. The low-temperature rubber elasticity may be
impaired when the heat of fusion according to DSC exceeds
30 J/g.

30 DSC is a method of measurement using a differential
scanning calorimeter (JIS K7121 and K7122).

The chlorine content of the obtained chlorinated
polyolefin is preferably 15-45 wt%, more preferably 20-40
wt% and even more preferably 25-35 wt%. If the chlorine
content is less than 15 wt% or above 45 wt%, the rubber
elasticity, and especially the low-temperature rubber
35 elasticity, may be impaired.

The elongation of the chlorinated polyolefin based
on a tensile test is preferably 1500% or greater and more

preferably 1600% or greater, and the glass transition temperature is preferably no higher than -25°C.

A chlorinated polyolefin obtained by the production process of the invention may be crosslinked as crosslinked rubber by being used in a composition comprising basically an acid acceptor, a reinforcer, a crosslinking agent and a plasticizer. The crosslinking may be accomplished by an ordinary method employing, for example, a press, injection molder, vulcanizer, hot air furnace or the like, selected as appropriate depending on the composition and the purpose of use.

The acid acceptor may be any one ordinarily used with chlorinated polyolefins. As examples there may be mentioned oxides or hydroxides of calcium, magnesium and the like, or synthetic hydrotalcite, synthetic zeolite or the like. These acid acceptors may be used alone or in combinations of two or more. The acid acceptor may be used in a proportion of 0.5-20 parts by weight and preferably 1-15 parts by weight to 100 parts by weight of the chlorinated polyolefin. If the acid acceptor is used at less than 0.5 part by weight the acid accepting function will be insufficient, while if it is used at greater than 20 parts by weight the obtained crosslinked rubber may have inferior mechanical strength.

As examples of reinforcers there may be mentioned carbon black, silica, calcium carbonate, talc, clay or the like. These may be used alone or in combinations of two or more. The reinforcer may be used in a proportion of 10-80 parts by weight and preferably 20-60 parts by weight to 100 parts by weight of the chlorinated polyolefin. If the reinforcer is used at less than 10 parts by weight the obtained crosslinked rubber may have inferior mechanical strength, while if it is used at greater than 80 parts by weight the flexibility may be impaired.

As examples of crosslinking agents there may be mentioned mercaptotriazine-based compounds,

mercaptobenzothiadiazole-based compounds, organic peroxides and the like.

As examples of mercaptotriazine-based compounds there may be mentioned 2,4,6-trimercapto-1,3,5-triazine, 5 1-methoxy-3,5-dimercaptotriazine, 1-hexylamino-3,5-dimercaptotriazine, 1-diethylamino-3,5-dimercaptotriazine, 1-cyclohexylamino-3,5-dimercaptotriazine, 1-dibutylamino-3,5-dimercaptotriazine and 1-phenylamino-3,5-dimercaptotriazine.

10 Crosslinking accelerators may also be used in combination with these mercaptotriazine-based compounds. As examples there may be mentioned basic accelerators such as basic amine compounds, basic amine organic acid salts or addition products or diarylguanidine, 15 sulfenamide accelerators, thiuram accelerators, and the like.

As examples of mercaptobenzothiadiazole compounds there may be mentioned 2,5-dimercapto-1,3,4-thiadiazole, 20 5-mercpto-1,3,4-thiadiazole-2-thiobenzoate, 1,3,4-thiadiazolyl-2,5-dithiobenzoate, 5-mercpto-1,3,4-thiadiazole-2-thiostearate, 5-mercpto-1,3,4-thiadiazole-2-thio-1-naphthoate, 5-mercpto-1,3,4-thiadiazole-2-thiophenylacetate, 5-mercpto-1,3,4-thiadiazole-2-thiocyclohexylcarboxylate, 5-mercpto-1,3,4-thiadiazole-25 2-thio-p-toluate, 5-mercpto-1,3,4-thiadiazole-2-thiocinnamate, 2,5-di(butoxymethyl)-1,3,4-thiadiazole, 2,2'-dimercapto-5,5'-dithiobis(1,3,4-thiadiazole) and 2,2'-di(butoxymethyl)-5,5'-dithiobis(1,3,4-thiadiazole).

As examples of organic peroxides there may be 30 mentioned ketone peroxide, peroxyketal, hydroperoxide, dialkyl peroxides, diacyl peroxide, peroxy esters and peroxy dicarbonate, and as specific examples there may be mentioned 1,1-bis(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, dicumyl peroxide, 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane, *n*-butyl-4,4-bis(*t*-butylperoxy)valerate and α,α' -bis(*t*-butylperoxy-*m*-isopropyl)benzene. These organic peroxides may be used

alone or in combinations of two or more.

Crosslinking aids may also be used in combination with these organic peroxides. As examples of useful crosslinking aids there may be mentioned diallyl 5 phthalate monomer, triallyl cyanurate, triallyl isocyanurate, ethyleneglycol dimethacrylate, trimethylpropane trimethacrylate and N,N'-*m*-phenylenebismaleimide. These coagents may also be used alone or in combinations of two or more.

10 The crosslinking agent may be used in a proportion of 0.5-10 parts by weight and preferably 1-5 parts by weight to 100 parts by weight of the chlorinated polyolefin. If the crosslinking agent is used at less than 0.5 part by weight, crosslinking may be insufficient 15 making it impossible to achieve the intended crosslinked rubber properties. If it is used at greater than 10 parts by weight, the viscosity may increase during working, not only constituting a hindrance for molding but also resulting in inferior flexibility of the 20 obtained crosslinked rubber.

As examples of plasticizers there may be mentioned phthalic esters such as dibutyl phthalate, diethyl 25 phthalate, diheptyl phthalate, di-2-ethylhexyl phthalate, di-*n*-octyl phthalate and dinonyl phthalate, aliphatic dibasic acid esters such as dimethyl adipate, diisobutyl adipate, dibutyl adipate, di-2-ethylhexyl adipate, diisodecyl adipate, dibutyldiglycol adipate, di-2-ethylhexyl azelate, dimethyl sebacate, dibutyl sebacate, 30 di-2-ethylhexyl sebacate and methylacetyl ricinoleate, and phosphoric acid esters such as trimethyl phosphate, triethyl phosphate, tributyl phosphate, tri-2-ethylhexyl phosphate, tributoxyethyl phosphate, trioleyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyldiphenyl phosphate, xylenyldiphenyl phosphate and 2-ethylhexyldiphenyl phosphate. These 35 plasticizers may also be used alone or in combinations of two or more.

The plasticizer may be used in a proportion of 5-70 parts by weight and preferably 10-60 parts by weight to 100 parts by weight of the chlorinated polyolefin. If the plasticizer is used at less than 5 parts by weight 5 the plasticizing effect may be inadequate, while if it is used at greater than 70 parts by weight bleeding of the plasticizer may occur.

In addition to the basic composition described above, other components may be appropriately added as 10 necessary, such as stabilizers, flame retardants, pigments, antioxidants, ultraviolet absorbers, processing aids and the like, which are commonly used in crosslinked rubbers and plastics.

In a cold flex test described in JIS K6261-1993 15 (Vulcanized Rubber Cold Flex Test), the temperatures at which the relative modulus (RM) of the obtained crosslinked rubber is 2, 5 and 10 (t_2 , t_5 and t_{10}) are $\leq -25^{\circ}\text{C}$, $\leq -40^{\circ}\text{C}$ and $\leq -45^{\circ}\text{C}$, respectively, and preferably $\leq -27^{\circ}\text{C}$, $\leq -43^{\circ}\text{C}$ and $\leq -49^{\circ}\text{C}$, respectively. The relative 20 modulus is the value with respect to the modulus at ordinary temperature ($23 \pm 2^{\circ}\text{C}$), and these values are the temperatures for a 2-fold, 5-fold and 10-fold modulus, respectively. A lower temperature here reflects a lower hardening temperature and thus more excellent low- 25 temperature properties as rubber, and it is common practice to select materials with reference to t_2 , t_5 or t_{10} depending on the purpose of use and the type of member. The numerical values are determined either from the modulus or the twist angle at numerous points as 30 measured continuously from a low temperature; a difference of $2\text{-}3^{\circ}\text{C}$ in the relative modulus thus means a higher modulus at each temperature in the low-temperature range and therefore higher rigidity at low temperatures, and is therefore generally considered to be a major 35 difference in terms of practical use.

The obtained crosslinked rubber maintains the heat

resistance of conventional chlorinated polyolefin-based crosslinked rubber, while exhibiting a satisfactory balance between excellent low-temperature rubber elasticity and high mechanical fatigue strength and 5 compression set, and it is therefore suitable for purposes including automobile parts, for example, boots such as constant velocity universal joint boots and hoses such as air cleaner hoses, or for industrial uses, for example, as hoses, sheets, packings and the like.

10 The present invention will now be explained in greater detail through examples and comparative examples, with the understanding that the invention is in no way limited by these examples.

15 The mean particle size was determined by measuring the filtered weight fraction by the Ro-Tap method using a wire sieve according to JIS Z8801, and recording the mean particle size as the particle size with a 50% cumulative weight percentage.

20 The melt flow rate (MFR) was measured at 190°C, according to JIS K7210.

25 In order to determine the crystal heat of fusion, crystal melting start temperature (T_{ms}) and crystal melting peak temperature (T_{mp}), the crystal heat of fusion was measured using a differential scanning calorimeter according to JIS K7121 and K7122, and the melting start temperature and peak temperature were read during the measurement.

30 The tensile strength and elongation were measured according to JIS K6301. The T_g (glass transition temperature) was measured according to the method described in Kobunshi Jikkengaku [Polymer Experiments] Vol.12, "Thermodynamic, electrical and optical properties" (Kyoritsu Publishing Co., Ltd.), p.74-77.

Example 1

35 Pellets of polyethylene NF-364A (density: 0.920, M_w/M_n : 2.0) by JPO Co., Ltd. (obtained by melting, kneading and pelleting polymerized powder) were

pulverized to a mean particle size of 0.45 mm (450 μm) using a turbogrinder by Turbo Kogyo Co., Ltd.

Next, 80 L of water, 80 g of sodium alkyldiphenylethersulfonate as a dispersing agent and 80 g of sodium polystyrenesulfonate as an anti-agglomerating agent were added to a 100 L autoclave, and 10 kg of the aforementioned pulverized polyethylene was loaded therein.

The first stage of chlorination was carried out to a chlorine content of 15 wt% at 105°C. The chlorine gas supply was then interrupted, heating to 127°C was followed by cooling to 110°C, and a second stage of chlorination was carried out to a chlorine content of 28 wt% at a temperature of 110°C. The chlorination was followed by water washing and drying by ordinary procedures to obtain chlorinated polyethylene. The crystal melting start temperature of the chlorinated polyethylene after the heat treatment step conducted between the first stage of chlorination and the second stage of chlorination was 85°C.

A test piece was prepared by adding 2 parts by weight of dioctyltin maleate and 1 part by weight of calcium stearate as stabilizers to 100 parts by weight of the chlorinated polyethylene, kneading the mixture for 5 minutes with a roll at 130°C and then press molding a test piece at a temperature of 170°C and a pressure of 200 kg/cm².

Examples 2-9

Chlorination was carried out in the same manner as Example 1 using the starting materials and conditions shown in Table 1, and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

Comparative Example 1

Chlorination was carried out in the same manner as Example 1 except that polyethylene powder with a mean

particle size of 400 μm (polymerized powder without melting or kneading) was used as the starting material without pulverization, and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

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Comparative Example 2

Chlorination was carried out using the same starting materials as Example 1 pulverized to 800 μm , and the obtained chlorinated polyethylene was used to fabricate a test piece in the same manner as Example 1.

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Comparative Examples 3 and 4

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The polyethylene of the polyethylene pellets used in Example 6 but before pelleting (the polymerized powder) was used as the starting material for Comparative Example 3 and the polyethylene of the polyethylene pellets used in Example 7 but before pelleting (the polymerized powder) was used as the starting material for Comparative Example 4, without melting or kneading, and performing only particle size adjustment by pulverization. The subsequent chlorination was carried out under the same conditions as in the respective examples and test pieces were fabricated.

Table 1

First step	Starting material properties						Chlorination step conditions						
	Melt-ing/ knead-ing before pulver- ization	Form before pulver- ization	Density g/cm ³	Mw/Mn	MFR g/10 min	Mean particle size μm	Tms °C	Tmp °C	First step	Second step	Tms after second step	Tempo- rature °C	Degree chlorina- tion wt%
Example 1 yes	pellet	0.920	2.0	1.0	450	75	126	105	15	127	85	110	28
Example 2 yes	pellet	0.920	2.0	1.0	420	75	126	105	15	127	86	110	28
Example 3 yes	pellet	0.920	2.0	1.0	100	75	126	105	15	127	88	105	28
Example 4 yes	pellet	0.920	2.0	1.0	100	75	126	105	15	127	88	110	28
Example 5 yes	pellet	0.920	2.0	4.0	400	74	125	105	15	126	87	110	28
Example 6 yes	pellet	0.912	2.5	2.0	440	71	124	105	15	125	86	110	28
Example 7 yes	pellet	0.930	2.6	1.0	400	73	125	105	15	126	87	110	28
Example 8 yes	pellet	0.920	2.0	1.0	450	75	126	110	10	127	88	110	28
Example 9 yes	pellet	0.920	2.0	1.0	450	75	126	105	15	127	85	115	28
Comp. Ex. 1 no	powder	0.920	2.0	1.0	400	74	126	105	15	127	87	110	28
Comp. Ex. 2 yes	pellet	0.920	2.0	1.0	800	75	126	105	15	127	88	110	28
Comp. Ex. 3 no	powder	0.912	2.5	2.0	440	71	124	105	15	125	85	110	28
Comp. Ex. 4 no	powder	0.930	2.6	1.0	400	73	125	105	15	126	86	110	28

The test pieces obtained by the method described above were used for measurement of properties such as crystal heat of fusion, tensile strength, elongation and Tg. The results are shown in Table 2.

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Table 2

	Properties of chlorinated product					
	Crystal heat of fusion J/g	Degree of chlorination wt%	M100 MPa	TB MPa	Elongation %	Tg °C
Example 1	1.0	28	1.20	6.06	≥1600	-25
Example 2	1.0	28	1.05	4.97	≥1600	-26
Example 3	10	28	1.04	3.62	≥1600	-25
Example 4	1.0	28	0.94	3.42	≥1600	-26
Example 5	1.0	28	1.20	6.00	≥1600	-25
Example 6	<0.1	28	0.85	5.54	≥1600	-27
Example 7	0.5	28	0.96	7.02	≥1600	-25
Example 8	1.5	28	1.09	6.25	≥1600	-25
Example 9	<0.1	28	0.94	6.14	≥1600	-26
Comp. Ex. 1	10	28	1.32	8.34	1200	-22
Comp. Ex. 2	1.0	28	2.50	10.00	1000	-20
Comp. Ex. 3	1.0	28	1.24	6.06	1200	-23
Comp. Ex. 4	2.0	28	1.65	7.43	1100	-20

10 The chlorinated polyethylene products obtained in Examples 1 to 9 all had elongation of 1600% or greater in the tensile test and a low 100% modulus, indicating high flexibility. Also, the glass transition temperatures were -25°C or below, indicating satisfactory low-temperature flexibility. On the other hand, the 15 chlorinated polyethylene products obtained in the Comparative Examples 1 to 4 had poor flexibility and glass transition temperatures exceeding -25°C, indicating poor low-temperature flexibility.

20 The following test was also conducted in order to examine the properties of the crosslinked rubber at low temperature.

To 100 parts by weight of the chlorinated polyethylene obtained in each of the examples and

comparative examples there were added 10 parts by weight
of magnesium oxide (KYOWAMAG 150-1, product of Kyowa
Chemical Industry Co., Ltd.), 50 parts by weight of
carbon black (SHOBLACK MAF·G, product of Showa Cabot,
5 KK.) and 40 parts by weight of a plasticizer (SANSOSAIZA-
DOS, product of New Japan Chemical Co., Ltd.), and the
mixture was kneaded with a Banbury mixer. After then
adding 2.5 parts by weight of 1,3,5-trithiocyanuric acid
(TCA-D, product of Ouchishinko Chemical Industrial Co.,
10 Ltd.) as a crosslinking accelerator and 1.5 parts by
weight of a dicyclohexylamine salt of 2-
mercaptobenzothiazole (MDCA, product of Ouchishinko
Chemical Industrial Co., Ltd.) as a crosslinking agent,
the mixture was kneaded with a roll.

15 For further crosslinking, the kneaded mixture was
pressed with a press at 180°C for 6 minutes and heated in
an oven at 150°C for 3 hours to obtain a sample.

The obtained crosslinked rubber samples were
subjected to a cold flex test according to JIS K6261
20 (Vulcanized Rubber Cold Flex Test), and the t_2 ,
temperature, t_5 temperature and t_{10} temperature of the
relative modulus (RM) were calculated. For measurement
of the mechanical fatigue property, pulling at a tension
from 0-100% was repeated 10 million times at a rate of
25 300 times/min using an elongation tester with 10 JIS #3
dumbbells, and the number of broken samples was recorded.
A smaller number of broken samples indicates a superior
mechanical fatigue property. The compressive set was
also measured according to JIS K6301, with 25%
30 compression at 100°C for 70 hours.

The results are shown in Table 3.

Table 3

	Crosslinked rubber properties					Number of broken samples from mechanical fatigue (of 10)	Compression set %		
	Cold flex test				Freezing point °C				
	t ₂ temperature °C	t ₅ temperature °C	t ₁₀ temperature °C						
Example 1	-28	-43	-49	-62		0	29		
Example 2	-32	-45	-51	-64		0	24		
Example 3	-28	-45	-50	-62		0	29		
Example 4	-30	-46	-52	-63		0	25		
Example 5	-28	-44	-49	-61		0	26		
Example 6	-33	-48	-55	-66		0	23		
Example 7	-30	-46	-51	-63		0	26		
Example 8	-30	-46	-51	-63		0	24		
Example 9	-31	-47	-51	-64		0	27		
Comp. Ex. 1	-24	-38	-42	-57		7	38		
Comp. Ex. 2	-23	-37	-41	-56		8	38		
Comp. Ex. 3	-24	-39	-43	-58		10	36		
Comp. Ex. 4	-21	-36	-39	-52		5	37		

The crosslinked rubbers of the chlorinated polyethylene obtained in Examples 1 to 9 had t₂, t₅ and t₁₀ temperatures of below -25°C, -40°C and -45°C, respectively, in the cold flex test with the Gehman tester, indicating excellent low-temperature flexibility. Also, the compression sets were below 30%, indicating a satisfactory balance with low-temperature flexibility. The mechanical fatigue properties also indicated superior durability judging from the small number of broken samples.

On the other hand, the crosslinked rubbers of Comparative Examples 1 to 4 had t₂, t₅ and t₁₀ temperatures of or above -25°C, -40°C and -45°C, respectively, in the cold flex test, indicating poor low-temperature flexibility. Also, the compression sets were greater than 30%, indicating poor balance with low-temperature flexibility, and the mechanical fatigue properties indicated inferior durability judging from the number of half or more broken samples.

Industrial Applicability

The present invention provides chlorinated polyolefins which can be used for the production of crosslinked rubbers and thermoplastic elastomers useful in the field of automobiles, household electrical 5 appliances, building materials and the like.

CLAIMS

1. A process for production of a chlorinated polyolefin comprising a step of melting and kneading a polyolefin and then molding it to obtain a solid, a step of pulverizing the solid into powder having a mean particle size of no greater than 500 μm , and a step of chlorinating the powder.

2. A process for production of a chlorinated polyolefin according to claim 1, wherein the chlorinating step further comprises a first step of chlorination at above the crystal melting start temperature and more than 10 $^{\circ}\text{C}$ below the crystal melting peak temperature of the polyolefin starting material as determined by DSC, a second step of interrupting the chlorine supply and performing heat treatment by heating to a temperature which is higher than 5 $^{\circ}\text{C}$ below the crystal melting peak temperature, and a third step of rechlorination at a temperature above the crystal melting start temperature of the chlorinated polyolefin after the heat treatment step.

3. A process for production of a chlorinated polyolefin according to claim 1 or 2, wherein the polyolefin is polyethylene.

4. A process for production of a chlorinated polyolefin according to claim 3, wherein the polyethylene is linear low-density polyethylene.

5. A process for production of a chlorinated polyolefin according to claim 3 or 4, wherein the density of the polyethylene is 0.90-0.93.

6. A process for production of a chlorinated polyolefin according to any one of claims 3 to 5, wherein the polyethylene is polyethylene with a weight-average molecular weight (M_w) and number-average molecular weight (M_n) ratio (M_w/M_n) of no greater than 3.0 as measured by gel permeation chromatography.

7. A chlorinated polyolefin produced by a process according to any one of claims 1 to 6, wherein the

chlorinated polyolefin has a crystal heat of fusion of no greater than 30 J/g according to DSC.

8. A chlorinated polyolefin according to claim 7, wherein the chlorine content is 15-45 wt%.

5 9. A chlorinated polyolefin according to claim 7 or 8, wherein the elongation based on a tensile test is 1500% or greater, and the glass transition temperature is no higher than -25°C.

10 10. A chlorinated polyolefin according to any one of claims 7 to 9, wherein the chlorinated polyolefin is chlorinated polyethylene.

) 11. A chlorinated polyolefin crosslinkable composition comprising 100 parts by weight of a chlorinated polyolefin according to any one of claims 7 15 to 10, 0.5-20 parts by weight of an acid acceptor, 10-80 parts by weight of a reinforcer, 0.5-10 parts by weight of a crosslinking agent and 5-70 parts by weight of a plasticizer.

20 12. A crosslinked chlorinated polyolefin obtained by crosslinking a chlorinated polyolefin crosslinkable composition according to claim 11.

) 13. A crosslinked chlorinated polyolefin according to claim 12, wherein the temperature at which the relative modulus (RM) = 2 by a cold flex test is no 25 higher than -25°C.

14. A crosslinked chlorinated polyolefin according to claim 12, wherein the temperature at which the relative modulus (RM) = 5 by a cold flex test is no higher than -40°C.

30 15. A crosslinked chlorinated polyolefin according to claim 12, wherein the temperature at which the relative modulus (RM) = 10 by a cold flex test is no higher than -45°C.

35 16. An automobile boot or hose employing a crosslinkable composition or crosslinked polyolefin according to any one of claims 11 to 15.

17. An industrial hose, sheet or packing employing

a crosslinkable composition or crosslinked polyolefin according to any one of claims 11 to 15.

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ABSTRACT

Uniform chlorinated polyolefins which can give crosslinked rubbers and thermoplastic elastomers with excellent low-temperature rubber elasticity, compression set and fatigue strength, and a process for their production. Polyolefin powder pulverized to a mean particle size of no greater than 500 μm is used for chlorination.